20030227190

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MENTATION PAGE

Form Approved
OMB No. 0704-0188

is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, ing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this ing this burden. to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson d to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	October 1992	Interim Technical Report

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
The Design and Construction of an Ion Trap Based System for Laser Pyrolysis/Mass Spectrometry of Single Organic Aerosol Particles	DAAL03-91-G-0296

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8. PERFORMING ORGANIZATION REPORT NUMBER

DTIC
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

ARO 29332.1-LS

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE
Approved for public release; distribution unlimited.	

13. ABSTRACT (Maximum 200 words)

This report describes the development of particle introduction techniques to support a 3 year program for analysis of single bacteria via laser pyrolysis/mass spectrometry. Results of an investigation into various sample introduction techniques are discussed including the highly successful quasi-electrospray introduction method using a suspension of particles in methanol. Particles from .9 to 13 μm have been levitated at pressures down to 10^{-7} torr, and mass spectrometry pressures of 10^{-3} torr have been obtained in less than 10 min from particle. The effectiveness of these techniques for particle introduction, pump down and stabilization has exceeded of the authors expectations and gives a positive prognosis for efforts to perform initial laser pyrolysis/mass spectrometry experiments in the year 2 effort.

93-03393

14. SUBJECT TERMS		15. NUMBER OF PAGES
		16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std 239-18
298-102

entitled:

The Design and Construction of an Ion Trap Based System for

Laser Pyrolysis/Mass Spectrometry of Single Organic Aerosol Particles.

Period Covered: 8/1/91 - 7/31/92

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I. Technical Overview

The development of an Ion Trap Particle Pyrolysis MS system is described in terms of 6 primary task areas which will be addressed in the course of a three year program. This report covers the developments during the period 8/1/91 to 7/31/92 which were slated to cover the first two tasks of particle introduction and particle containment (see Table I). Additionally, task 3 of particle imaging and stabilization has been addressed in connection with verifying particle containment.

TABLE I
TIME PLAN

	YEAR 1				YEAR 2				YEAR 3			
Task 1: (Sample Introduction)	X	X	X	X	.	.	.	.	.	.	.	.
Task 2: (Particle Containment)	.	.	X	X	X	X	.	.	.	.	.	.
Task 3: (Imaging and Stabilization)	.	.	.	.	X	X	.	.	.	.	.	.
Task 4: (Laser Pyrolysis/Desorption)	.	.	.	.	.	X	X	X	X	.	.	.
Task 5: (MS Detection)	.	.	.	.	.	.	.	.	X	X	X	X
Task 6: (Biocompound Analysis)	.	.	.	.	.	.	.	.	.	X	X	X
Task 7: (Reporting)	.	.	.	X	.	.	.	X	.	.	.	X

If these first year tasks are seen as connected, the primary goal of the year 1 effort has been to develop the particle levitation system to the point where a particle may be introduced, taken to high vacuum, and returned to introduce the next particle within 15 minutes. A greater

than 4 sample per hour system throughout is desired recognizing that the sample introduction and pump down is that rate limiting step for the full pyrolysis MS experiment. Having achieved this goal, it would be desirable that the procedure require as little operator intervention as possible so that it may be readily automated.

Several sample introduction methods were investigated. The most productive, due to its highly effective particle charging mechanism, was a quasi-electrospray technique where particles were introduced into the system from an alcohol suspension via a charged spray from a high voltage needle. The vacuum system is then rapidly pumped from ambient pressure, which yields, effective initial trapping conditions, to high vacuum. The ability to achieve this pumpdown in under 10 minutes was a major program success. (The expected pumpdown time from atmosphere of 30-45 minutes was the primary incentive for reduced-pressure sample introduction.)

It is further believed that the authors have achieved the first system capable of investigation the trajectories of particles in an ion trap at pressures low enough to offer insight into the behavior of ions at vacuum pressures. Trajectory sizes and responses to various excitations may offer new insights into the behavior of Ion Trap resolution enhancements via axial excitation as well as excitations used for collision induced dissociation in Ion Trap MS/MS scans. These insights will benefit both the stabilization efforts of task 3, and the biological analyses needed in tasks 5 and 6.

II. Technical Description

The principal objective of the year 1 effort was to introduce the sample particle into the vacuum system with sufficient charge that if may be trapped and rapidly stabilized under high

vacuum conditions (10^{-3} Torr) required for Ion Trap MS. Obtaining this objective required a means for sample introduction which would allow a changed aerosols to be directed into the Ion Trap which was operating in Electrodynamic Balance (EDB) mode. If the particles were appropriately introduced, in terms of initial velocity and electrical charging, they would be trapped and their position would be verified by means of a microscopic video imaging system. For this reason, all three initial tasks (sample introduction, particle containment and particle imaging/stabilization) were to be closely related in the year 1 program.

Initial work on sample introduction focused an means to introduce aerosol particles suspended in a gas stream into the EDB system. Mr. Arnold visited Dr. Asit Ray at the University of Kentucky who has been developing EDB techniques for over 10 years in the study of optical scattering and weight loss properties of aerosol particles. In particular he had performed a number of experiments at reduced pressure which could offer insights for this experiment. In his experience, pump downs to a few torr required about 1/2 to 1 hour because air movements during pumpdown destabilized the particles. He could not address additional problems that might come at high vacuum conditions. In his work all sample introduction had been performed at atmospheric pressure, but it appeared from this visit that sample introduction at reduced pressure would be required to speed up this pumpdown process, if sufficient sample throughput was to be maintained. A number of additional notes on equipment configuration and construction were also obtained.

A modeling effort was pursued to evaluate the ability to introduce particles at reduced pressures suspended in a gas stream. Use of a capillary restrictor for sample introduction was established in several existing aerosol introduction MS experiments [1,2] but these experiments

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did not require deceleration of the particle in the vacuum environment. A model based upon the assumption of Hagen-Poiseuille flow in the capillary and Stokes Law drag on the particle was utilized to predict conditions required to decelerate the particles in the EDB system at reduced pressure.
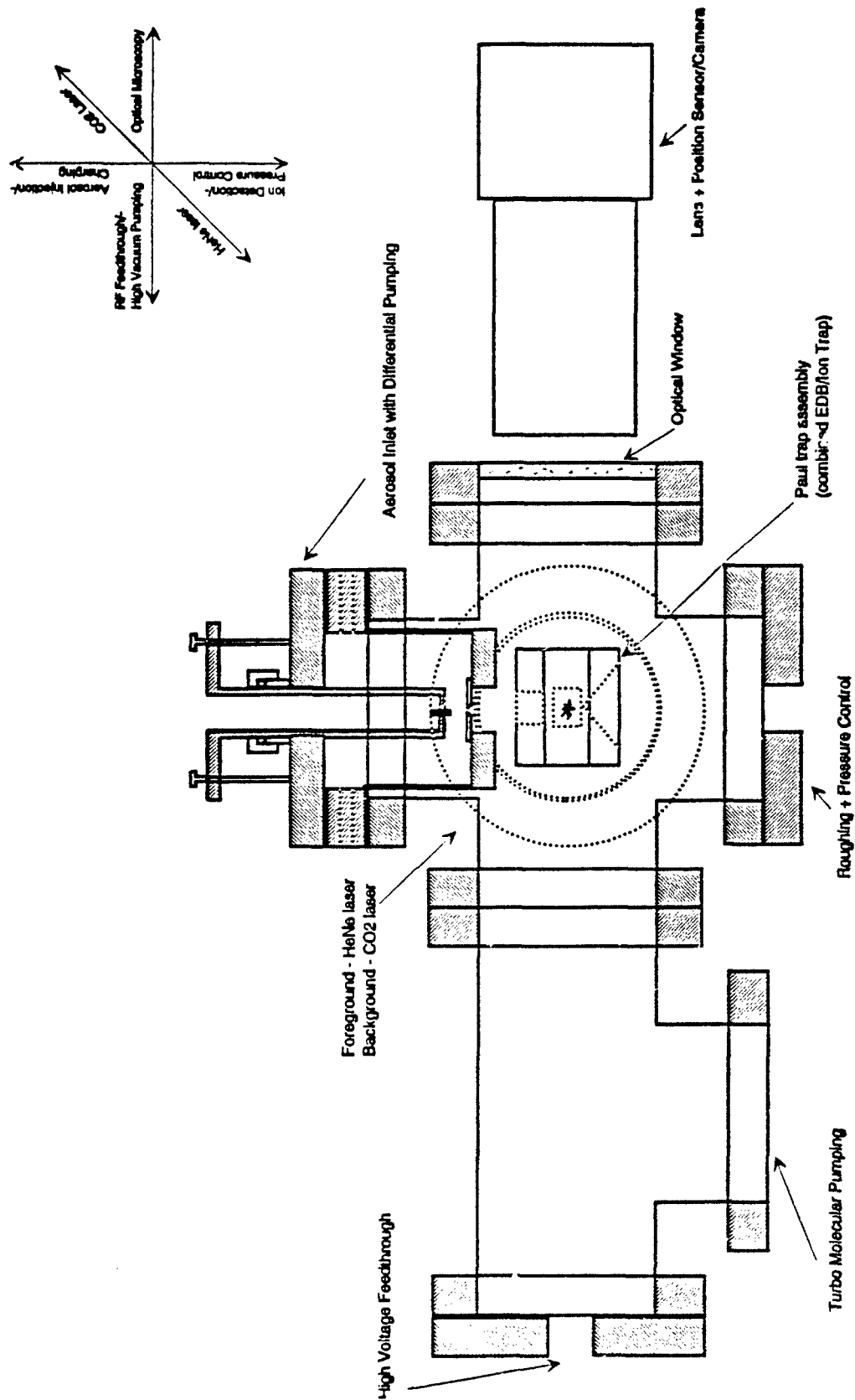
Figure 1 illustrates the effect of pressure on particle damping of various particle sizes. Delta is the damping factor of the particle motion (the inverse of the decay time constant). The reduced pressure environment produces reduced damping of the particle, and a reduced trapping probability. These damping factors are then coupled with the capillary restrictor particle velocities obtained from the model in Figure 2. The stopping distance of the particle is determined by its capillary outlet velocity divided by delta. The characteristic dimensions of the EDB provide an estimate of acceptable pressures for particle injection. An EDB radius of 1 cm provides an estimate that pressures between 1/10 and 1/100 atmosphere may still yield efficient trapping while providing a significantly reduced starting pressures for pumpdown to high vacuum conditions. As the apparatus for initial testing (Figure 3) was completed, several levitation tests were performed at atmospheric pressure to begin to evaluate issues around charging and particle damping which were not addressed in the model. In particular, the model yielding the curves in Figure 2 assumes a sharp transition from the particle entrainment in the capillary flow into a region of damping in "still" air in the trap which in practice appears very difficult to obtain. Further, the charging efficiency will affect both the voltages required to initially trap the particle and the susceptibility of the particle to destabilization due to eddy currents of air in the trapping region.

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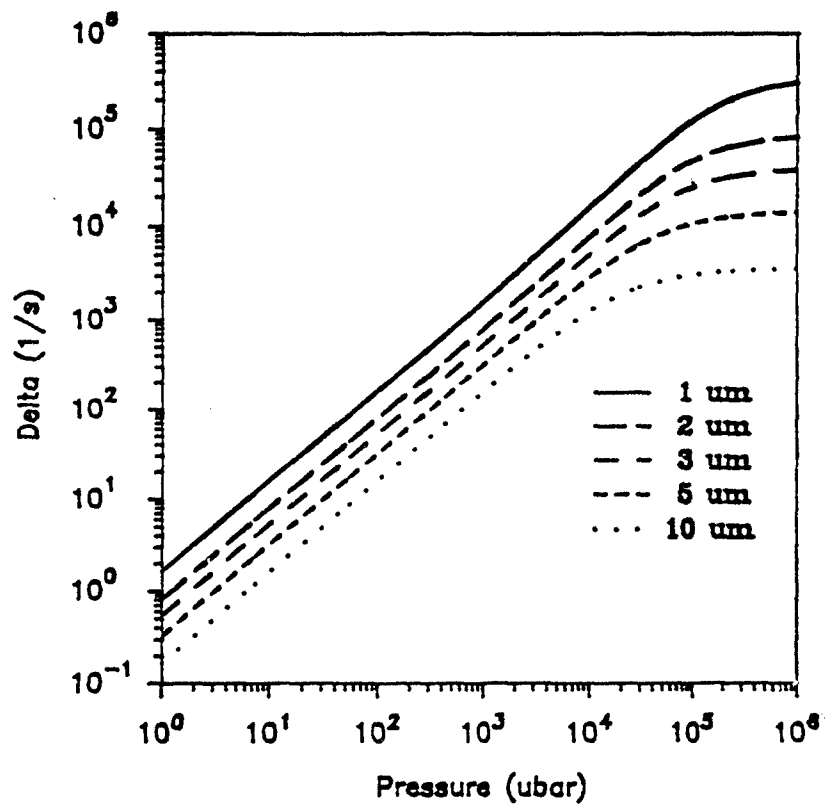
1. Particle damping factor as a function of gas pressure. Computed for air at 20 C.

50 um capillary
.5 cm long
——— 1 um
— – – 2 um
— – 5 um
– – – 10 um
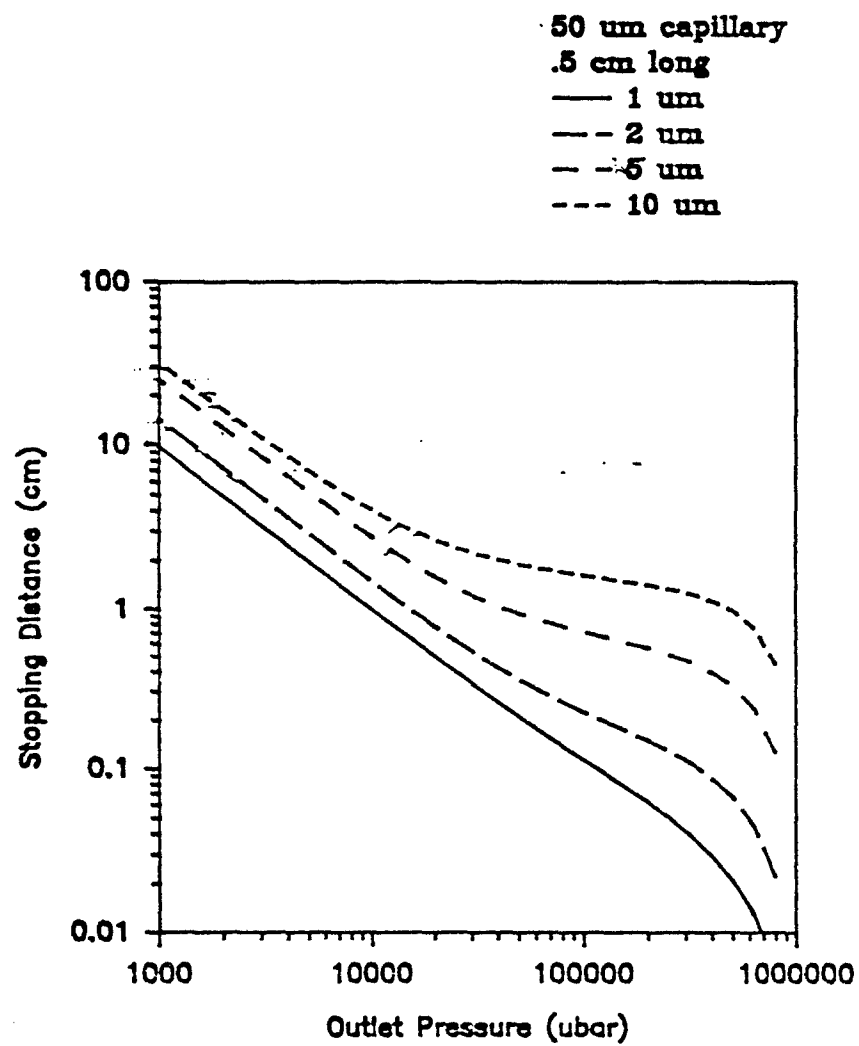
2.   Particle stopping distance as a function of capillary outlet pressure for aerosol injection

model.

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Optical Microscopy

CO2 Laser

Ion Desorption-
Pressure Control

Aerosol Injection-
Charging

RF Feedthrough-
High Vacuum Pumping

HeNe laser

Lens + Position Sensor/Camera

Aerosol Inlet with Differential Pumping

Optical Window

Paul trap assembly
(combined EDB/Ion Trap)

Foreground - HeNe laser
Background - CO2 laser

Roughing + Pressure Control

High Voltage Feedthrough

Turbo Molecular Pumping

3.   Particle levitation apparatus.

These initial efforts were troubled by insufficient and erratic charging of test particles. Poorly controlled variables such as system humidity contributed to the erratic nature of charging but more troubling were the high voltages required to trap particles generated by electrostatic means. These voltages, in excess of 3 KV, would readily discharge at reduced pressures destabilizing the particle and would not be compatible with high vacuum pumpdown. In order to perform vacuum experiments, it appeared that lower m/z ratios would be required. Our typical values at this time were in the range of 2×10^{11} daltons per elemental charge.

Comparison with m/z values obtained calculated from Richardson [3] for reduced pressure levitation experiments indicated that target m/z values are on the order of 10^9 daltons per charge. For a 10μm particle, this implies 3×10^5 charges would be required which is well beyond the field charging limit of the particle even in a 5 KV/cm electric field. (Even a 1μm particle is right at this limit with the 300 charges required to give 10^9 daltons per charge.) With this information, it was clear that only a very sophisticated solution for particle charging was compatible with gas phase particle introduction.

Rather than pursue this further, an alternative mechanism for charging was proposed which is based upon an analogy with electrospray techniques. In this case, an injector was constructed from a syringe and a high voltage power supply. A 26.5 ga needle, cut off and polished, formed the spray tip and particles were introduced into the syringe as a suspension in methanol. This approach has yielded highly reproducible results for particle charging which lead to high injection efficiencies. This technique allows initial droplet size and charge to be controlled. The primary variables include field strength, solvent characteristics and needle size.

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Utilizing a specific needle size, geometry and solvent, the voltage is adjusted to give a desired initial droplet size which is slightly larger than the particle size (so that the mass does not decrease much during evaporation). And the charge level is approximately at the Rayleigh limit. This allows nearly 10^6 charges on a 10μm particle.

Although the electrospray droplet is accelerated by large electric fields at the needle tip, the atmospheric damping yields a large number of trapped particles from a single pulse of liquid (a few μL). More importantly, these particles have a high immunity to destabilization by air drafts within the system. This allows the system, at relatively low trapping voltages (<100 V p-p), to be pumped from atmosphere to 10^{-3} torr in less than 5 min. This extraordinary stability has eliminated the need for reduced pressure sample introduction! Further, this stability has eliminated the need for computer based, electrical stabilization systems which were originally envisioned during pumpdown.

It is believed that 10^{-3} torr will be a sufficiently low system pressure to perform the laser pyrolysis and mass spectrometry on a particle. If lower pressures are required, stabilization of various particles, including 13 μm paper mulberry pollen, latex microspheres to .93μm and bacillus subtillus spores, have been obtained at pressures down to 10^{-7} torr, but achieving these pressures requires special measures to contain the size of the particle trajectory and to remove condensate (primarily H_2O) in the vacuum system that limits pumpdown speed below 10^{-3} torr. The latter will be limited by venting the system back to atmospheric pressure with dry air.

The expansion of particle trajectories below 10^{-3} torr is due primarily to thermal and electrical noise which is no longer damped out by the gas damping forces. In this region the "Matthieu" trajectories are readily observed (see Figure 4). It is not clear if these trajectories
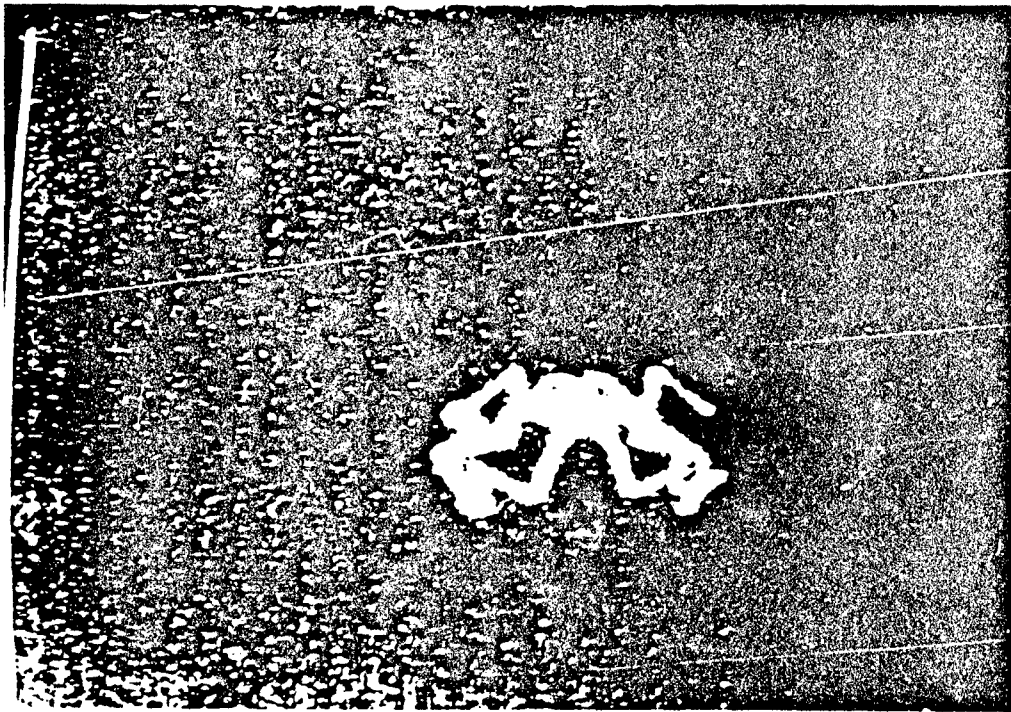
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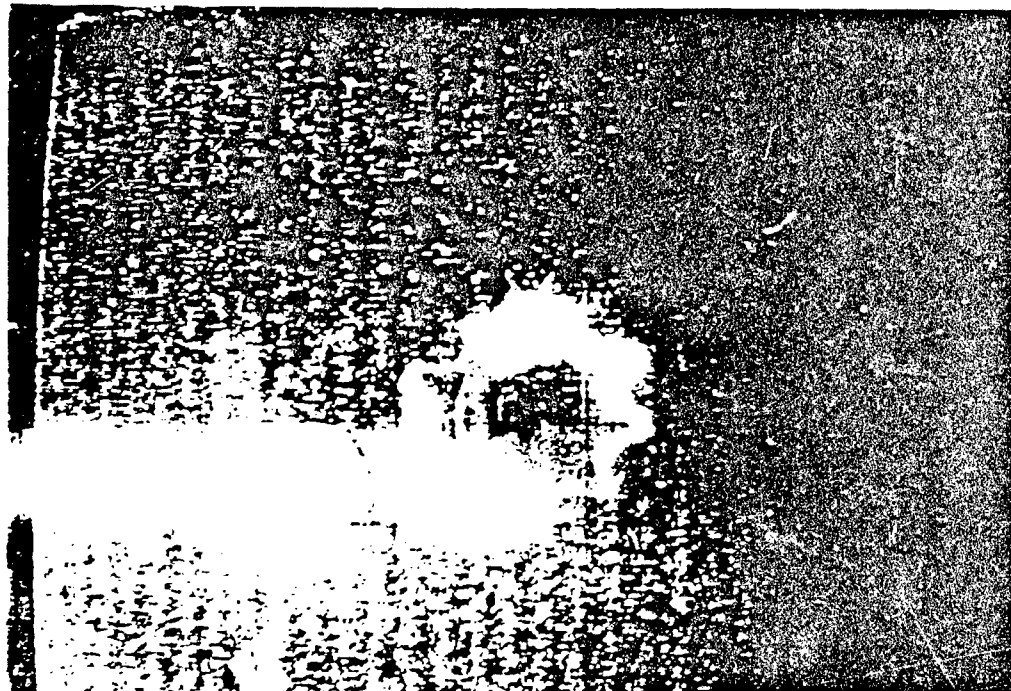Figure 4a. An example particle trajectory photographed through the trap ring.

Figure 4b. An example particle trajectory photographed through the top end cap.

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may be damped by electrical means, but initial efforts indicated that if damped by pressures on the order of 10^{-3} torr, the particle can be stabilized back at the center of the trap. Expansion of the trajectory after such a damping may take several minutes, so that gas leaks provide an effective stabilization mechanism compatible with high vacuum pyrolysis experiments.

It was anticipated that the position would be less localized at reduced pressure and that additional means would be necessary to maintain the particle at the trap center for laser targeting. It was not anticipated that it would be so stable to such a low pressure. The ability to trap particles under these conditions has provided a new opportunity to study "ion trajectories" as a function of pressure and trapping conditions. Pursuit of this area could provide valuable insights into resolution enhancements provided by resonance ejection [4] and into the process of collision induced dissociation in Ion Trap MS instruments. Both of these areas are of importance to tasks 5 and 6 in analysis of the biological materials produced by laser pyrolysis/desorption.

III. Technical Prognosis

These results of the year 1 efforts yield a very positive prognosis for single particle mass spectra from pyrolysis of biological materials. The ability to trap and detect single organisms at MS pressures has been demonstrated, and the system appears fast enough to do a large number of MS experiments. At present a CO_2 laser system is being set up for initial pyrolysis of trapped particles. The greatest challenge of the year 2 effort will be the transition from EDB to Ion Trap MS field conditions.

The ion trapping RF levels may be started at any time since they don't affect the trapped particles, but the particle trapping EDB fields will destabilize ions created by the pyrolysis. If

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the EDB fields can be shut off in <10 ms, the laser may be fired after the EDB fields are off and before the particle falls from the trap. Present equipment designs appear to allow for this, but some modifications may be required.

Continuing developments in tandem Ion Trap mass spectrometry also enhance the prognosis for this experiment. A related experiment in our laboratory has demonstrated MS/MS spectra of many parent ions from a single direct probe vacuum pyrolysis experiment. The ability to record multiple daughter spectra to yield characteristic information on bacteria promises to impact the ability to obtain similar information from a single bacteria in the present experiment.

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